



TITLE:

High pressure transition in cadmium selenide

AUTHOR(S):

Onodera, Akifumi

CITATION:

Onodera, Akifumi. High pressure transition in cadmium selenide. The Review of Physical Chemistry of Japan 1970, 39(2): 65-77

ISSUE DATE:

1970-04-10

URL:

<http://hdl.handle.net/2433/46934>

RIGHT:

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 39, NO. 2, 1969

HIGH PRESSURE TRANSITION IN CADMIUM SELENIDE

BY AKIFUMI ONODERA

The wurtzite—rock salt phase boundary of a single crystal of cadmium selenide was investigated experimentally over the P , T range up to 25 kb and 700°C by observing the electrical resistance behavior in a cubic compact anvil device.

In single crystal samples the room temperature transition pressure is found to be 24.7 ± 1.6 kb. At the transition the electrical resistance decreases by several orders of magnitude. The transition pressure is lowered with increasing temperature. The wurtzite—rock salt phase boundary has a slope of -0.012 kb/deg. The heat of transition at room temperature calculated from the Clapeyron equation is 5.0×10^2 cal/mole. The change in entropy is found to be 1.7 e.u.

Both the atmospheric wurtzite phase and the high-pressure rock salt phase are semiconductors. From the measurements of electrical resistance as a function of temperature it is found that the energy gap of CdSe of the wurtzite phase is about 1.6 eV. For the CdSe of the rock salt phase the energy gap obtained is about 0.6 eV.

Introduction

Cadmium selenide (CdSe) occurs under the normal conditions in two modifications, one having the hexagonal wurtzite structure and the other having the cubic zinc blende structure. The cubic modification of CdSe was discovered in thin layers^{1)~3)} or in precipitants from aqueous solutions⁴⁾. It was found⁴⁾ that the cubic modification was transformed into the hexagonal by heating at 100~200°C. However, Semiletov found⁵⁾ that the cubic phase increased on heating the CdSe films containing both modifications. No data on the stability relations of the two modifications at atmospheric pressure have been available as is the case of CdS and AgI in the same modifications.

It has been shown by the optical absorption⁶⁾, the electrical resistance⁷⁾⁸⁾, and the volume change⁹⁾¹⁰⁾ measurements that CdSe undergoes a phase transition under a pressure of 20~30 kb. The transition is accompanied by a large discontinuous red shift in the optical absorption edge and a corresponding increase by several orders of magnitude in the electrical conductivity. Jayaraman *et al.*⁹⁾

(Received December 10, 1969)

- 1) J. Yamaguchi and S. Katayama, *J. Phys. Soc. Japan*, **5**, 386 (1950)
- 2) S. Nagata and K. Agata, *ibid.*, **6**, 523 (1951)
- 3) M. Aoki and S. Tanaka, *Oyo Butsuri (J. Appl. Phys. Japan)*, **24**, 113 (1955)
- 4) A. S. Pashinkin and R. A. Sapozhnikov, *Soviet Phys.—Cryst.*, **7**, 501 (1962)
- 5) S. A. Semiletov, *Kristallografiya*, **1**, 306 (1956)
- 6) A. L. Edwards and H. G. Drickamer, *Phys. Rev.*, **122**, 1149 (1961)
- 7) S. Minomura, G. A. Samara and H. G. Drickamer, *J. Appl. Phys.*, **33**, 3196 (1962)
- 8) C. J. M. Rooymans, *J. Inorg. Nucl. Chem.*, **25**, 253 (1963)
- 9) A. Jayaraman, W. Klement, Jr. and G. C. Kennedy, *Phys. Rev.*, **130**, 2277 (1963)
- 10) C. F. Cline and D. G. Stephens, *J. Appl. Phys.*, **36**, 2869 (1965)

have studied the compression of the powdered samples using a piston-cylinder apparatus and reported a volume decrease of about 9 per cent at the transition. Cline and Stephens¹⁰⁾, using single crystal samples in a piston-cylinder apparatus, have reported a volume decrease of about 16 per cent at the transition.

Recently the direct identification of the high pressure phase of CdSe has been briefly reported¹¹⁾¹²⁾. In these cases, the identification was achieved by means of high pressure x-ray cameras. It is agreed that the high pressure phase of CdSe has the cubic NaCl (rock salt) structure.

No previous investigation of the effect of temperature on the transition pressure of CdSe from the wurtzite to the rock salt structure has been reported, although the melting curve of CdSe up to about 15 kb has been reported by Jayaraman *et al.*⁹⁾ using the differential thermal analysis method.

This investigation was undertaken in order to determine the wurtzite—rock salt phase boundary of CdSe at high pressures and high temperatures. The observation of discontinuities in the pressure dependence of the electrical resistance under isothermal conditions was used to define the boundaries of the two solid phases. Furthermore, the temperature dependence of the conductivity of the wurtzite and the high-pressure rock salt phases was investigated and the energy gaps were estimated.

Experimentals

The experiments were performed by using a cubic compact anvil high-pressure apparatus¹³⁾, and the details of the experimental methods were fully discussed in the previous publications¹⁴⁾¹⁵⁾. Only some specific items will be presented here. The cubic compact anvil press was calibrated for the cell pressure in terms of applied press force by substituting bismuth, thallium or barium for the CdSe in the cell and observing the known pressure-induced transitions in these elements in accordance with Kennedy and LaMori's scale¹⁶⁾. No correction was made for the effect of elevated temperature on the pressure calibration. The assembly for internal heating and sample encapsulation as shown in Fig. 1 was the same as described previously¹⁴⁾¹⁵⁾ except for the following modifications: first, the graphite was used instead of the glassy carbon; second, polyethylene tubes sheathing the thermocouple were not inserted into the pyrophyllite cube. The cylindrical sample was enclosed in the center of pyrophyllite cube, the edges of which were 13.0 mm long. The electrical contacts were made at the two ends of the sample through platinum foils. The graphite cylinder served as the heat source as the result of joule heating due to the passage of a high-current through it. The nominal outside diameters of the cylindrical sections of the sample cube were: (1) sample, 2 mm; (2) pressure transmitting cylinder, 4 mm; and (3) graphite heating core, 6 mm. There was no apparent reaction between

11) C. J. M. Rooymans, *Phys. Letters*, **4**, 186 (1963)

12) A. N. Mariano and E. P. Warekois, *Science*, **142**, 672 (1963)

13) J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *This Journal*, **34**, 1 (1964)

14) J. Osugi, K. Shimizu, T. Nakamura and A. Onodera, *ibid.*, **36**, 59 (1966)

15) J. Osugi, K. Shimizu, T. Nakamura and A. Onodera, *ibid.*, **36**, 74 (1966)

16) G. C. Kennedy and P. N. LaMori, "Progress in Very High Pressure Research", ed. by F. P. Bundy *et al.*, p. 304~311, John Wiley & Sons, New York (1961)

the CdSe and pyrophyllite or platinum foils in the temperature and pressure range covered.

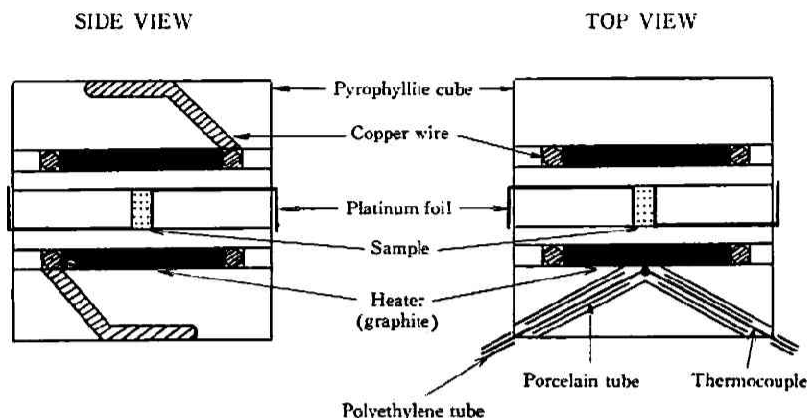


Fig. 1 Sample configurations for resistance measurements in cubic anvil apparatus

Temperatures were measured with the chromel-alumel thermocouple which had been calibrated against the melting points of tin, lead, zinc and aluminum. The corrections of the measured temperatures for the effect of pressure on the thermocouples were made in accordance with the results reported by Hanneman and Strong¹⁷⁾.

The CdSe samples (wurtzite form) for the electrical resistance measurements were cut from the Eagle Picher 'ultra high pure' single crystal. Optical analysis indicated that the purity was supposedly 99.999 per cent, the main impurities being Mg, Si, and Al. Measurements were also made at room temperature on the powder samples of the wurtzite form of 99.99 per cent purity, and on the zinc blende form of 99.99 per cent purity.

The experimental points of wurtzite—rock salt phase boundary of single crystals of CdSe were obtained by raising the pressure in small increments at the definite temperature. Discontinuity in the pressure dependence of the electrical resistance defines the boundaries of two solid phases. The data were obtained at temperatures from room temperature to 700°C on different samples.

The energy gaps were estimated by the measurements of the temperature dependence on electrical conductivity at constant pressures. The isobars of resistance as a function of temperature were measured at three different pressures in the wurtzite phase, and at two different pressures in the rock salt phase.

The electrical resistance measurements were reduced to absolute resistivity values by measuring the dimensions of the samples at room conditions after the runs. It was not possible, however, to obtain resistivity values at the end of every experiment. The samples usually shattered, and their final measurement was not possible. For this reason the data are given in terms of relative values only.

17) R. E. Hanneman and H. M. Strong, *J. Appl. Phys.*, **36**, 523 (1965)

Results

Pressure-temperature phase diagram

The measurements on room temperature resistance *versus* pressure were performed on single crystals (wurtzite form), and on the powder samples of both wurtzite and zinc blende forms. Fig. 2 shows the results for the single crystal and the powder samples. The initial resistivities were $\sim 6 \times 10^4 \Omega \cdot \text{cm}$ for single crystals and $\sim 5 \times 10^6 \Omega \cdot \text{cm}$ for powder samples. For pressures up to about 20 kb the electrical resistance increases with pressure. In the single crystal samples the transition of wurtzite-to-rock salt occurs at $24.7 \pm 1.6 \text{ kb}$ accompanied by a sharp decrease in resistance of over four orders of magnitude. In the powder samples of wurtzite form the transition takes place at about 29 kb. The difference in the transition pressure between the single crystal and powder samples has been also observed for the transition in $\text{CdSi}^{14)}$. The behavior of the powder sample of the zinc blende form was rather different. The transition starts at much higher pressure, and the order of the magnitude in the resistance drop is much smaller. The resistivities of the rock salt phase transformed from the wurtzite form were $\sim 10^{-2} \Omega \cdot \text{cm}$ and that from the zinc blende form was $\sim 10^1 \Omega \cdot \text{cm}$, respectively, at about 70 kb. There is a marked hysteresis effect in these curves, as has been observed for the transition in $\text{CdSi}^{14)}$.

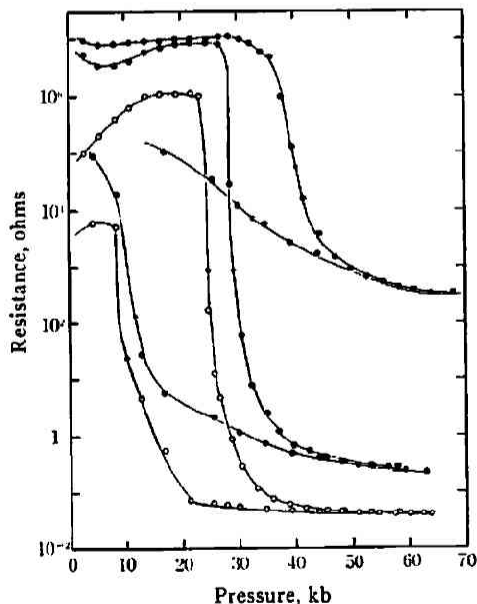


Fig. 2 Resistance *versus* pressure for CdSe at room temperature

○: single crystal (wurtzite form)
●: powder (wurtzite form)
⊙: powder (zinc blende form)

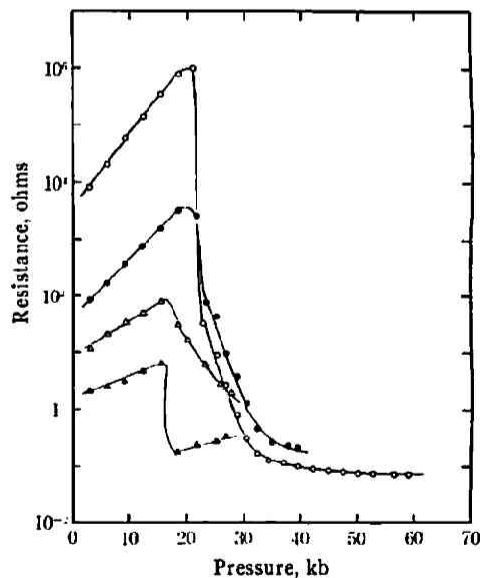


Fig. 3 Resistance *versus* pressure isotherms of single crystals of CdSe

○: 100°C ●: 200°C
△: 500°C ▲: 700°C

The pressure of the wurtzite-to-rock salt transition in CdSe at room temperature is compared with the previous investigations^{6)~10)} in Table 1. Drickamer and his colleagues used the same material in their optical⁶⁾ and electrical⁷⁾ studies.

Table 1 Pressures of the wurtzite-to-rock salt transition in CdSe

Investigator	P_T (kb)	Method	Reference
Present work	24.7 ± 1.6	electrical resistance	
Minomura <i>et al.</i>	34	electrical resistance	7
Rooymans	22-23	electrical resistance	8
Jayaraman <i>et al.</i>	23	volume change	9
Cline and Stephens	21.3 ± 0.8	volume change	10
Edwards and Drickamer	27	optical absorption	6

The boundary between the wurtzite and the rock salt structures of CdSe was determined by keeping the single crystal samples at constant temperature and increasing the pressure. The typical isotherms are shown in Fig. 3. The electrical resistance of the wurtzite phase increases with increasing pressure at any temperature. The phase diagram can be obtained from the data of Fig. 3, and the result is shown in Fig. 4. The points were obtained on the assumption that the phase boundary was the pressure at which the resistance started to decrease. The transition pressure is lowered by increasing temperature, dP/dT being -0.012 kb/deg. This negative slope was predicted in the previous paper¹⁴⁾. The volume change at the transition, using the lattice constant (5.54 \AA) of the rock salt phase of CdSe obtained from the x-ray diffraction analysis¹¹⁾ and the volume of the wurtzite phase of CdSe

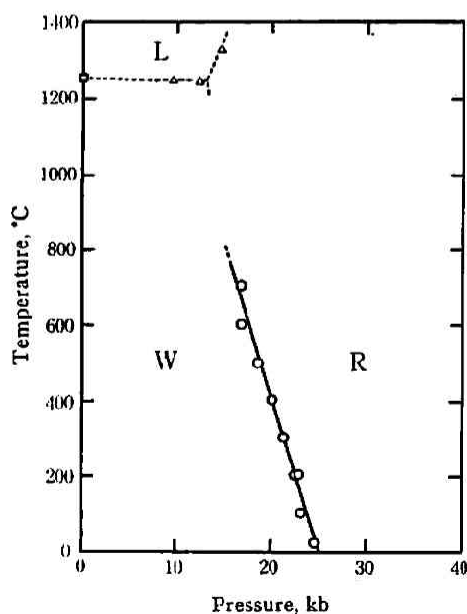


Fig. 4 Phase diagram of wurtzite (W)
—rock salt (R) structures of
CdSe
○: present work
△: Jayaraman *et al.*

corrected for the compressibility¹⁰⁾, is $-6.2 \text{ cm}^3/\text{mole}$. Since the values are now available for dP/dT and for the volume change ΔV , accompanying the transition, we can calculate the enthalpy change ΔH , and the entropy change ΔS , accompanying the transition from the Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V} \quad (1)$$

The change in enthalpy is found to be $5.0 \times 10^2 \text{ cal/mole}$ and in entropy to be 1.7 e.u.

In Fig. 4 are plotted the melting data of Jayaraman *et al.*⁹⁾ from the differential thermal analysis studies, and from the knick point of the melting curve it was proposed that the triple point between the liquid and two solid phases would be at about $13 \pm 1 \text{ kb}$ and $1,252^\circ\text{C}$. It seems most probable that the wurtzite—rock salt transition line will meet the triple point.

Attempts were made to retain the rock salt phase of CdSe. The method has been described earlier¹⁰⁾. For both single crystal and powder samples (initially in the wurtzite form) the experiments were run between 35 and 50 kb and between room temperature and 900°C for 1~12 hours in the stability field of the rock salt phase in the P, T phase diagram of CdSe given in Fig. 4. All the recovered samples were characterized by using the standard powder x-ray diffraction techniques. In single crystals of CdSe the x-ray diffraction patterns showed the lines which corresponded to mixtures of the zinc blende and wurtzite phases, the zinc blende structure being predominant. In powder samples of CdSe the diffraction patterns showed the lines corresponding to only the zinc blende

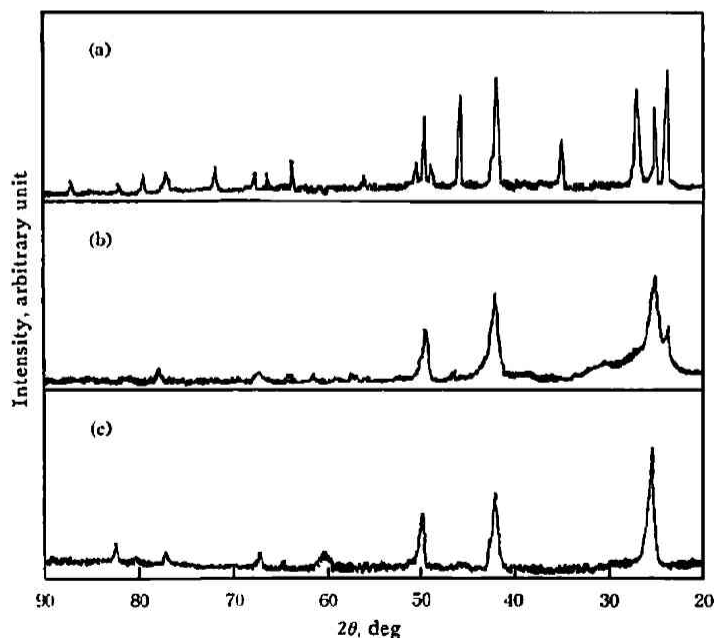


Fig. 5 Examples of x-ray diffraction patterns for CdSe
 (a) atmospheric wurtzite form
 (b) sample held at 45 kb and 400°C for 2 hr
 (c) atmospheric zinc blende form

structure, or the mixture of the zinc blende and wurtzite. In Fig. 5 are reproduced some examples of x-ray diffraction patterns on strip-chart recorder with $\text{CuK}\alpha$ radiation. The patterns (a) and (c) are those of atmospheric wurtzite and zinc blende forms of CdSe , respectively. The pattern (b) was recorded for the sample which had been started from the single crystal and treated at 45 kb and 400°C for 2 hr, showing the zinc blende structure to be predominant. In several samples, an extra line was observed at about $2\theta=31.2^\circ$. This could not be assigned to either element Cd or Se, which might be brought about, if occurred, by the decomposition of the CdSe sample. Table 2 summarizes the pressure-temperature data for quenching treatment in CdSe . Besides those listed in Table 2, experiments were performed at room temperature. The samples which had been placed under 50 kb for 2 or 12 hours at room temperature were mixture of the zinc blende and wurtzite in both the single crystal and powder samples. The lines in the diffraction patterns of the pressurized samples were much broader than in the patterns of the samples which had not been compressed. This suggests that the high pressure transition may introduce a much smaller particle size. The diffraction patterns of the pressurized samples showed no change after the duration of one month at atmospheric pressure and at room temperature, and after being annealed in air for 2 hr at the temperature of 200°C . By further annealing in air for 4 hr at 400°C , the zinc blende form was transformed into the wurtzite form. For comparison, the non-pressurized samples of the wurtzite and zinc blende form were heated in air for 2 hr at 200°C , and further for 4 hr at 400°C . The wurtzite form remained unchanged after the both treatments. The zinc blende form was transformed into the wurtzite form after being heated at 400°C for 4 hr. The result agrees with the pressurized sample. The trend of the structural change of CdSe at high temperature and at atmospheric pressure, as shown above, agrees with the result reported by Pashinkin and Sapozhnikov⁴⁾.

Table 2 Pressure-temperature data for quenching treatment

Pressure (kb)	Temperature ($^\circ\text{C}$)	Time of duration (hr)	Results Z: Zinc blende W: Wurtzite
Single crystal sample			
40	800	3	Z+W
45	400	2	Z+W
50	200	2	Z+W
Powder sample			
35	300	2	Z+W
35	600	1	Z+W
35	600	2	Z+W
50	200	2	Z
50	400	2	Z
50	400	4	Z+W
50	400	6	Z+W
50	600	3	Z+W
50	900	2	Z

The effect of particle size

As is shown in Fig. 2 a marked difference was observed in the transition pressures between single crystal and powder samples of CdSe. The results in Fig. 2 and CdS¹⁴⁾ lead to the experiments to find whether the particle size would affect the transition pressure of CdSe. Single crystal was crushed to particles in an agate mortar. It was confirmed by the x-ray diffraction that the wurtzite structure did change neither to the zinc blende nor to the rock salt structure during grinding. The average diameters of the classified samples were determined by means of an electron microscope. The wurtzite-to-rock salt transition pressures observed by electrical resistance measurements are shown in Fig. 6. The transition pressure increases with the decrease in the particle size. The result will again serve to illustrate how the particle size might affect the transition.

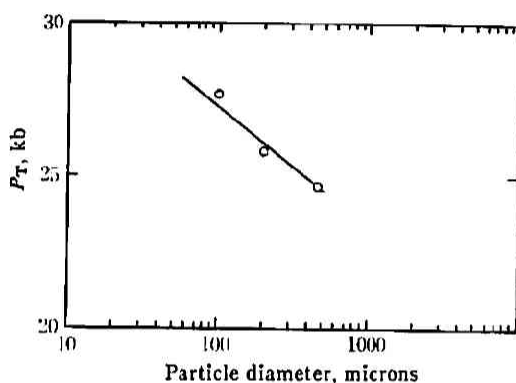


Fig. 6 Transition pressure of coarse-grained particles as a function of particle diameter

Pressure cycling

As mentioned above, the high-pressure phase of CdSe mostly showed the mixture of zinc blende and wurtzite structures on release of pressure after room temperature experiments. The recovered sample of a mixture of zinc blende and wurtzite form was recompressed at room temperature. This was done by starting with a single crystal of wurtzite form of CdSe, compressing it into the rock salt structure, decompressing it into the mixture of zinc blende and wurtzite structure, and then recompressing to the rock salt form, and so on. The resistance as a function of pressure is shown in Fig. 7. The transition pressure on the second compression ②, zinc blende/wurtzite \rightarrow rock salt, was slightly higher than that of the first compression ①, wurtzite \rightarrow rock salt. The pressures of the transitions observed on the third and fourth compressions ③, ④ were higher than those observed on the first and second compressions. After the fourth compression ④, the recovered sample to the atmospheric pressure was examined by x-ray diffraction and found to be the pure zinc blende structure. The results suggest that the transition pressure of each compression might be roughly dependent on the portion of the zinc blende form in the sample, the more the zinc blende form the higher is the transition pressure. The result of the x-ray diffraction analysis, as noted above, shows that the zinc blende form of CdSe can be obtained from the wurtzite form merely by the pressure cycling at room temperature.

Electrical resistance changes

Three isobars of resistance as a function of temperature were measured in the wurtzite phase of

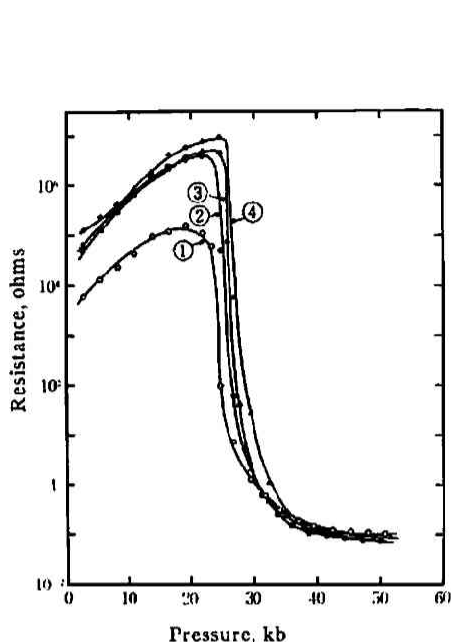


Fig. 7 Resistance versus pressure behavior of CdSe during compression cycles (①→②→③→④)

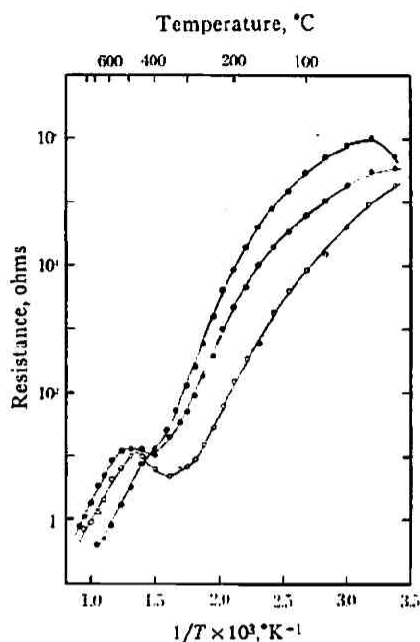


Fig. 8 Resistance versus $1/T$ isobars of CdSe of the wurtzite phase
○: 6.1 kb ●: 12.3 kb
◐: 18.5 kb

CdSe single crystals. The electrical resistance R , in the intrinsic region of conduction, is given by

$$R = R_0 \exp(E_g/2kT), \quad (2)$$

where E_g is the energy gap, k is the Boltzmann constant, T is the absolute temperature, and R_0 is an essentially temperature-independent constant. Then

$$E_g = 2k \frac{\partial \ln R}{\partial (1/T)}. \quad (3)$$

The slope of $\log R$ versus $1/T$ curves yields the energy gap. Fig. 8 shows the isobars of $\log R$ versus $1/T$. The three isobars are from different samples. The data in Fig. 8 yield for the energy gap of the wurtzite structure a value of $E_g = 1.6$ eV at 6.1, 12.3 and 18.5 kb. The intrinsic region of conduction is above about 500°C. This value is favorably compared with the atmospheric value of about 1.7~1.9 eV obtained from the optical data^{18)~20)} and the electrical resistance measurements²¹⁾. Within experimental uncertainty no variation of the energy gap with pressure could be detected in this study. The shift of the absorption edge of CdSe of the wurtzite phase with pressure was measured by Edwards and Drickamer⁶⁾ who found a pressure coefficient of 3.7×10^{-6} eV/bar. Grynberg²²⁾ measured the

18) R. H. Bube, *Phys. Rev.*, **98**, 431 (1955)

19) R. H. Bube, *ibid.*, **99**, 1105 (1955)

20) C. Konak and V. Prosser, *Czech. J. Phys.*, **14**, 559 (1964)

21) H. Tubota, *Japanese J. Appl. Phys.*, **2**, 259 (1963)

22) M. Grynberg, *Phys. Stat. Sol.*, **27**, 255 (1968)

optical absorption of CdSe under uniaxial stress at 77°K and 300°K, and reported the pressure coefficient of energy gap $(7.1 \pm 0.5) \times 10^{-6}$ eV/bar at 77°K, and $(6.3 \pm 0.5) \times 10^{-6}$ eV/bar at 300°K, respectively.

Fig. 9 shows the two isobars of $\log R$ versus $1/T$ in the rock salt phase of CdSe. The electrical resistance increases slightly near room temperature, but develops a strong positive temperature coefficient at higher temperature. Above about 300°C the resistance decreases exponentially with temperature, a behavior typical of semiconductor. The data in Fig. 9 yields for the energy gap of the rock salt structure a value of $E_g = 0.63$ eV at 33.3 kb, and $E_g = 0.62$ eV at 42.2 kb, giving the pressure coefficient of -1.1×10^{-6} eV/bar. Edwards and Drickamer⁶⁾ measured the shift of the optical absorption edge of CdSe in the high-pressure phase, finding a pressure coefficient of energy gap $dE_g/dP = -1.5 \times 10^{-6}$ eV/bar. The observed decrease in E_g with pressure in the present work is in agreement with the optical work⁶⁾.

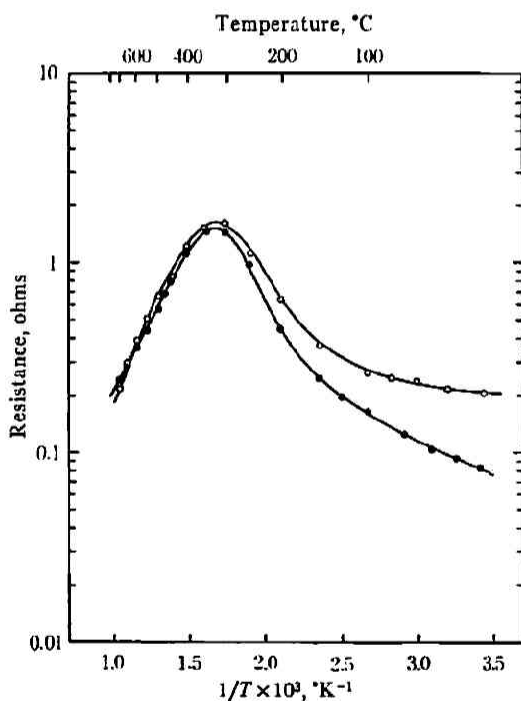


Fig. 9 Resistance versus $1/T$ isobars of CdSe of the rock salt phase
○: 33.3 kb ●: 42.2 kb

Considerations

Structural considerations

It is apparent that the reverse phase transition in CdSe is predominantly accompanied by a transition from the rock salt structure to the zinc blende structure. In CdS the sequence of transition, rock salt \rightarrow zinc blende \rightarrow wurtzite was observed on release of pressure¹⁴⁾. When the pressure is lowered the cadmium ions return to a tetrahedral position from the octahedral position of the rock salt

structure. Insufficient mobility of sulphur ions may result first in a zinc blende lattice and then in a wurtzite lattice in CdS. Since the selenium ions are less mobile than the sulphur ions because of the larger ionic size, CdSe may result more easily in the zinc blende than the wurtzite structure on release of pressure. When heated in air at atmospheric pressure, the selenium ions may become mobile and then return to a tetrahedral position, thus resulting in the wurtzite structure.

The effect of particle size

The effect of particle size has been observed on the pressures of wurtzite-to-rock salt transition in CdS in the previous paper¹⁴⁾ and in CdSe in the present work. Jacobs observed by the x-ray diffraction analysis under high pressure that the transition in RbI²³⁾ and in CsClO₄²⁴⁾ were more likely to occur in large crystals than in small ones, and that there was an appreciable subdivision of grains in a pressure transition.

On the contrary, Smith, King and Gebbie²⁵⁾ reported that, in the study of the transition of InSb from the zinc blende to the white tin structure by the electrical resistance measurements, the transition behavior began at lower pressure in a polycrystalline specimen than in a single crystal. The inference made was that the larger number of lattice defects in the polycrystalline specimen would provide the centers or the nuclei for the initiation of the transition, while in the relatively perfect single crystal the lack of such centers would inhibit the transition until high pressures be reached.

On the other hand, no apparent effect was observed in the crystallinity of the sample of CdTe on the pressure of the transition from the zinc blende to the rock salt structure²⁶⁾. The transition pressure was not altered in coarse-grained particles, and was not either altered in the pressure cycling experiments.

It could not be considered that these behaviors merely indicated the reflexion of pressure-dependent electronic transport in the polycrystalline samples, regarding that the observations were reported in both the cases of the lowering and the raising effects of the transition pressure in the polycrystalline specimen and the experiments were performed in electrical resistance measurements or x-ray diffraction methods.

In cadmium chalcogenides, as noted above, the effect of particle size has been observed in the wurtzite-to-rock salt transitions of CdS and CdSe, and not observed in the zinc blende-to-rock salt transition of CdTe. The wurtzite structure belongs to the hexagonal crystal system, and the zinc blende and rock salt structures belong to the cubic. The difference of stacking arrangement between the hexagonal and cubic structures has been discussed in the previous paper¹⁴⁾. The wurtzite-to-rock salt transition may be considered to occur by way of the martensite-type mechanism caused by shear¹⁴⁾. The effect of particle size on the transition pressure has been discussed in one of the previous papers¹⁴⁾ on the basis of thermodynamic considerations applicable to the transformation of martensite-type. The transition from the wurtzite to the rock salt structure cannot take place at a

23) R. B. Jacobs, *Phys. Rev.*, **54**, 468 (1938)

24) R. B. Jacobs, *ibid.*, **54**, 325 (1938)

25) P. L. Smith, J. H. King and H. A. Gebbie, "Physics and Chemistry of High Pressure", p. 140, Society of Chemical Industry, London (1963)

26) A. Onodera, *This Journal*, **39**, 78 (1969)

pressure where the chemical free energy difference $\Delta F^{W \rightarrow R}$ becomes negative. Here

$$\Delta F^{W \rightarrow R} = F^R - F^W. \quad (4)$$

The superscripts W and R refer to the wurtzite and the rock salt phases, respectively. The reason for the necessity of over-pressure is that the non-chemical free energy $\Delta G^{W \rightarrow R}$, such as interfacial energy and strain energy, opposes the transition. The interfacial energy is associated with the regions where new interfaces are produced when the transition takes place. The strain energy is mainly a consequence of the shear-like nature of the transition. The condition for transition to occur is

$$\Delta F^{W \rightarrow R} + \Delta G^{W \rightarrow R} < 0. \quad (5)$$

The non-chemical free energy decreases with increasing size of particles as discussed in the previous paper¹⁴⁾. Therefore it could be expected that a large wurtzite particle is more likely to transform into the rock salt phase than a small one. In the transition of zinc blende-to-rock salt structure in CdTe, however, the non-chemical free energy term may be small. For example, the strain energy may not need to be taken into account from the lack of shear-like behavior. Hence the effect of particle size may be small in CdTe.

The high-pressure phase of CdSe

The rock salt phase of CdSe was first believed²⁾ to be metallic because of the positive temperature coefficient of electrical resistance in the temperature range between 25° and 120°C. Jayaraman *et al.*, however, have raised the question and considered that the rock salt phase of CdSe might be non-metallic²⁷⁾. As shown in Fig. 9, the behavior of the resistance of CdSe of the rock salt phase suggests that the CdSe of the rock salt phase is still a semiconductor, and below about 300°C the conductivity is in the extrinsic region in this work.

No data concerned with the energy gap of the rock salt phase of CdSe have been reported, although its pressure dependence has been measured by Edwards and Drickamer⁶⁾ as cited earlier. It was shown experimentally for several semiconductors that the energy gaps were small when the resistivities were low²⁸⁾. The resistivity of CdSe of the rock salt phase is $\sim 10^{-2} \Omega \cdot \text{cm}$ as described above, and that of CdS of the same phase¹⁴⁾ is $\sim 10^1 \Omega \cdot \text{cm}$. Accordingly the observed value of about 0.6 eV in the rock salt phase of CdSe is considered to be reasonable since that of CdS of the rock salt phase is about 0.8 eV¹⁵⁾ or 1.3 eV²⁹⁾.

It was found that in semiconductor tellurium the metallic phase was introduced at about 40 kb when the energy gap decreased to zero³⁰⁾. The transitions from the insulating state to the conducting state in thallous halides were observed by the electrical resistance measurements at the pressures under which the energy gaps obtained from the optical works became zero³¹⁾. Likewise the rock salt phase of CdSe may be expected to transform into the conducting state as the result of the diminishing of the

27) See Ref. 9) and the reference 18 therein.

28) W. Meyer and H. Neldel, *Phys. Z.*, **38**, 1014 (1937)

29) G. A. Samara and A. A. Giardini, *Phys. Rev.*, **140**, A388 (1965)

30) F. A. Blum, Jr. and B. C. Deaton, *ibid.*, **137**, A1410 (1965)

31) G. A. Samara and H. G. Drickamer, *J. Chem. Phys.*, **37**, 408 (1962)

energy gap, which would be caused by the overlap of the energy bands. The estimated pressure under which the energy gap of the CdSe of the rock salt phase would diminish to zero is about 600 kb, assuming that no further phase transition may occur. Some remarks about the possibility of further phase transition in CdSe will be presented in the following paper²⁶⁾.

Acknowledgment

The author wishes to express his sincere thanks to Professor Jiro Osugi for his encouragement and advice during the course of this investigation. He also wishes to acknowledge Dr. Kiyoshi Shimizu for reviewing the manuscript and making many valuable criticisms. Thanks are due to Mr. Morio Inoue of Matsushita Elec. Co. for providing the single crystal used in this work.

*Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto, Japan*